

## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Improved Method of Manufacturing Calcium Carbonate

We, ECUSTA PAPER CORPORATION, a Corporation of the State of Delaware, United States of America, of Pisgah Forest, North Carolina, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

10 Our invention relates to the production of calcium carbonate and more especially to obtaining calcium carbonate of the proper size particles to serve as a filler for cigarette paper and impart to the  
15 paper the desired porosity and opacity characteristics.

Although this calcium carbonate may be used for other purposes, it is particularly adapted for use as a filler in  
20 cigarette paper. If the particles of calcium carbonate are too small, that is, if the calcium carbonate has too high a proportion of fine particles, its use as a filler in cigarette paper will result in  
25 paper less porous than desired, for the permissible amount of filler in the paper. *Contra*, if the particles of calcium carbonate filler are too large or coarse the paper will not have sufficient opacity.

30 Heretofore, it has been a major commercial problem to produce calcium carbonate filler within the exacting requirement for good porosity and opacity in cigarette paper. The difficulty has  
35 been the lack of any definite control over the particle sizes of the precipitated calcium carbonate. These sizes would vary widely from one production to the next and there seemed to be no reliable  
40 way to produce each batch within predetermined specifications. Successive productions would have unpredictable particle size distributions and oftentimes a batch of the calcium carbonate so produced could not be used satisfactorily as  
45 filler for the cigarette paper.

Our research was directed to an understanding of this problem and to the development of a reliable method for

consistently producing calcium carbonate 50 of the desired particle sizes. This result has been finally achieved by the method of our present invention.

According to the present invention there is provided a process for converting 55 a calcium carbonate having a minor proportion by weight of particles larger than 2 microns into a calcium carbonate having a major proportion by weight of particles larger than 2 microns, comprising firstly 60 preparing in a manner known *per se* an aqueous suspension of the calcium carbonate having a minor proportion by weight of particles larger than 2 microns, and secondly modifying the size of the 65 particles thus produced by introducing into said suspension controlled amounts of calcium hydroxide and carbon dioxide thereby effecting precipitation therefrom of additional calcium carbonate in the 70 presence of said suspension of calcium carbonate and continuing said precipitation until the calcium carbonate has a major proportion, by weight, of particles larger than 2 microns. 75

Other factors being constant, the degree of "coarsening," or diminishing the percentage of small particles, mentioned above, depends upon the amount of calcium carbonate precipitated in the 80 presence of the initial fine calcium carbonate. For the production of a final calcium carbonate of given average particle size, the finer the initial calcium carbonate the more calcium hydroxide 85 must be precipitated in its presence in order to produce any given average particle size for the entire batch. Conversely, if the initial calcium carbonate is less fine, less calcium carbonate must be 90 precipitated in its presence in order to obtain the given average particle size for the entire batch.

By sampling the batch, after the conditioning precipitation has progressed for 95 some time, and testing the samples for particle size, we can terminate the precipitation process at the time when the

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proportion of fine particles have been reduced to the desired extent.

In the commercial practice of our invention, we have found it advantageous to carry out the conditioning precipitation or coarsening process in batches, that is, to complete the precipitation, and then remove the entire batch of precipitated calcium carbonate from the carbonator.

If desired, the conditioning precipitation method may be carried out continuously, instead of in batches, and the final precipitated calcium carbonate drawn off continuously. In such a procedure it is

necessary to introduce continuously during the conditioning precipitation a supply of the previously prepared calcium carbonate suspension having fine particles so that the subsequent precipitation will be carried out in the presence of this previously produced fine product.

In carrying out our process for coarsening calcium carbonate particles according to a continuous method, we may use one, two, or more carbonators. Where more than one carbonator is used, we prefer to have the carbonators in series, i.e., to flow the initial calcium carbonate suspension through the system from one carbonator to the next in the series, and to divide among the carbonators the lime which is to be carbonated in the presence of the calcium carbonate initially present.

The fine particle size calcium carbonate with which we start may be obtained in several ways. Among the methods of preparing fine carbonate are the following: precipitation from calcium hydroxide suspension by reaction with carbon dioxide under predetermined conditions of concentration, temperature, and agitation; vigorous agitation of a calcium carbonate suspension, after precipitation; wet-milling of calcium carbonate; dry-grinding of precipitated calcium carbonate followed by air separation.

A commercially advantageous procedure for the preparation of this fine particle calcium carbonate suspension comprises, first, producing slaked lime, and then precipitating this slaked lime solution with carbon dioxide gas. A specific, non-limiting example of this procedure is as follows:

#### SLAKING

2,330 pounds of regular commercial grade, pebble size, rotary kiln quick lime (CaO) obtained from Mississippi Lime Company were charged into a tank containing 733 gallons of water initially at 95° C. The lime was added at a substantially uniform rate over a period of about 25 minutes. After the lime had all been added, the contents of the tank were

agitated for  $\frac{1}{2}$  hour by means of a stream of compressed air. The contents of the tank were then diluted to 1,000 gallons with filtered river water. Agitation was continued for another  $\frac{1}{2}$  hour, whereupon the suspension was passed through a coarse screen, about  $\frac{1}{4}$  inch mesh, then through a fine screen, about 100 mesh, and was finally pumped through a centrifugal cleaner to remove mechanical impurities.

#### CARBONATING

833 gallons of the above slaked lime were pumped into a tank approximately 5 feet in diameter and 10 feet high. The concentration of this suspension was adjusted to 180 grams of  $\text{Ca}(\text{OH})_2$  per liter, and the temperature to 40° C. Washed, boiler-house, flue gas, containing approximately 10% carbon dioxide, was now fed into the milk of lime at the rate of about 600 cubic feet per minute. This carbonating treatment was continued for 12 hours, after which time substantially all the  $\text{Ca}(\text{OH})_2$  in the tank had been converted to  $\text{Ca}(\text{OH})_2$ .

The calcium carbonate produced in the above example had a higher proportion of fine particles than we desired in a filler to be used in the manufacture of an important type of commercial cigarette paper. The particle size distribution of this calcium carbonate, as determined with an Andreasen Pipette, and using sodium hexametaphosphate as dispersing agent, was as follows:

Particle Sizes	Per Cent. by Weight	
0-1 microns	28%	105
1-2 microns	52%	
2-3 microns	8%	
3-4 microns	4%	
4-6 microns	3%	110
6-8 microns	3%	
9-10 microns	2%	
above 10 microns	0%	
	100%	

The weight-average particle size of this calcium carbonate was 1.8 microns.

The Andreasen Pipette is a standard piece of laboratory apparatus which can be purchased from many scientific supply houses. In the preparation of the sample to be examined with the pipette, we introduce a volume of slurry containing approximately 2 grams of solids and then add distilled water to the dilution mark on the pipette provided for the purpose. The distilled water used for diluting purposes contains approximately 0.15 grams of sodium hexametaphosphate dissolved therein. The function of the sodium hexametaphosphate is to disperse

the calcium carbonate so as to insure free settling.

To convert the fine particle, calcium carbonate suspension, prepared as above described, to one containing a substantially lower percentage by weight of fine particles, in accordance with our invention, we subjected the suspension to our conditioning precipitation method as follows:

#### CONDITIONING PRECIPITATION

We diluted the calcium carbonate suspension to 140 grams of solids per liter. 41½ gallons of this suspension was pumped into a tank 2 feet in diameter and 10 feet high. The tank was then about ¼ full. We next fed into this suspension or slurry a slow stream of milk of lime having a concentration of 100 grams per liter of calcium hydroxide. This lime was added at approximately 1½ gallons per minute, which was sufficient to maintain the free lime content in the carbonating mixture at about 6 grams per liter, expressed as  $\text{Ca}(\text{OH})_2$ . The total amount of lime thus added was 58½ gallons.

Simultaneously with the addition of this milk of lime, we fed in, at the bottom of the tank, washed flue gas containing 10% carbon dioxide at the rate of about 200 cubic feet per minute. The temperature of the carbonating mixture was approximately 30° C.

From time to time during this conditioning carbonation we removed samples of the precipitated calcium carbonate from the carbonating tank and tested them for particle size. As a convenient and rapid testing method, we measured the turbidity of a dilute suspension of the calcium carbonate under standardized conditions. When the percentage of fine particles in the precipitate had been reduced to the desired extent, we cut off the supply of milk of lime and continued the supply of washed flue gas for a few minutes until practically all of the free lime had been converted into calcium carbonate.

The particle sizes and percentages thereof resulting from this conditioning precipitation, or final carbonation, described above, are as follows:

Percentage Sizes	Per Cent. by Weight
0—1 microns	6%
1—2 microns	24%
2—3 microns	40%
3—4 microns	20%
4—6 microns	5%
6—8 microns	2%
8—10 microns	2%
above 10 microns	1%
	100%

By comparing the percentages of different particle sizes just above with those present in the original, fine calcium carbonate shown previously above, it will be noted that the extremely fine particles, i.e., those 0—1 microns in diameter, have been reduced in amount from 28% in the initial calcium carbonate to 6% in the total precipitate; and the next size, still very fine, particles 1—2 microns in diameter, have been decreased in amount from 52% to 24%. Similarly, the amount of particles larger than 2 microns has been increased from an original percentage of 20% to 70%, all as a result of the conditioning precipitation mentioned above. As a matter of identification, therefore, our process may be regarded as one for converting a calcium carbonate, having a minor proportion by weight of particles larger than 2 microns in size, into a calcium carbonate having a major proportion by weight of particles larger than 2 microns. Furthermore, it will be noted from the percentages given just above that while the particle sizes have been increased by this conditioning precipitation, the increase in size has been controlled substantially within the relatively narrow range below 4 microns, and there is only a minor percentage, e.g., 10%, of particles having a size greater than 4 microns. As a matter of fact the final carbonate, produced as above described, consists principally of particles between 2 and 4 microns in size, the percentage of these by weight in the above typical case being 60%.

It will be noted from the above, that the original calcium carbonate, which we used for converting or coarsening into the final carbonate, was very fine, although it was not colloidal, since it consisted predominately of particles 1 to 2 microns in size. There are many times larger than colloidal particles, which, according to definition, are within the size range of

1 to 1000 micron. While we might

possibly start with colloidal calcium carbonate and coarsen it sufficiently to produce the type of calcium carbonate which we desire for use in cigarette paper, for example, one having a major proportion of particle sizes above two microns and usually between 2 and 4 microns, we prefer not to start with a calcium carbonate this fine. Our process may be carried out entirely satisfactorily by starting with a calcium carbonate having a major proportion of particle sizes between 1 and 2 microns, as shown in the first table above.

As indicated above we may obtain the

fine, starting calcium carbonate material for our process from any suitable source. In practice, we have found it advantageous to prepare this carbonate by precipitation with carbon dioxide of a slaked lime solution under predetermined conditions of time, temperature, concentration, agitation, etc. Adventitious variations in the particle size frequency distribution characteristics of various batches thus prepared are compensated for by our method of conditioning, in which this precipitated calcium carbonate is subjected to the influence of a second precipitation of slaked lime with carbon dioxide, which second precipitation is carried out in an aqueous suspension of this previously precipitated calcium carbonate. This commercially advantageous, though non-restrictive, process of our invention may thus be considered as a two-stage, or two-step, precipitation process and is thus referred to hereafter.

In this two-stage precipitation process, a small percentage of the lime used in the first stage may be left unreacted. Thus, we have found it convenient to leave up to about 5% of the total slaked lime unreacted in the first stage precipitation in order to save time, since the carbonation usually slows down considerably when almost all of the lime has been carbonated. In carrying out the second step, or conditioning precipitation, we ordinarily continue the introduction of carbon dioxide into the carbonator after the supply of calcium hydroxide has been discontinued, until the residual, unreacted calcium hydroxide, which is present in the carbonator when the supply of calcium hydroxide is discontinued, has been neutralized.

In the conditioning precipitation step, we have found it expedient and effective to add the lime to the particles of calcium carbonate undergoing conditioning or coarsening at a rate such that, at any moment, unreacted calcium hydroxide is present in the carbonator in amount within the range of, say, about 1% to, say, about 25% of the weight of total calcium carbonate present. If the percentage of unreacted lime falls below 1%, the process tends to be, generally speaking, unduly slow. If the percentage increases substantially above 25%, we find that the desired control of the particle size is difficult and that the process approaches, from the standpoint of difficulty of control, a conventional carbonating process in which no fine calcium carbonate is used as a starting material.

To facilitate control in the conditioning step, we prefer to have the milk of

lime being added to the carbonating apparatus at a concentration equivalent to the concentration of the calcium carbonate suspension undergoing coarsening. Under this condition, the concentration of total calcium carbonate in the treating system manifestly remains constant.

When the final carbonation is completed, the precipitated calcium carbonate may be filtered and dried, or it may be used directly in slurry form, as a filler for paper by admixture with the paper furnish.

Various modifications may be made in the above described materials and procedures without departing from the scope of our invention as defined in the appended claims.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for converting a calcium carbonate having a minor proportion by weight of particles larger than 2 microns into a calcium carbonate having a major proportion by weight of particles larger than 2 microns, comprising firstly preparing in a manner known *per se* an aqueous suspension of the calcium carbonate having a minor proportion by weight of particles larger than 2 microns, and secondly modifying the size of the particles thus produced by introducing into said suspension controlled amounts of calcium hydroxide and carbon dioxide thereby effecting precipitation therefrom of additional calcium carbonate in the presence of said suspension of calcium carbonate and continuing said precipitation until the calcium carbonate has a major proportion, by weight, of particles larger than 2 microns.

2. A method as defined in claim 1 and in which the initial calcium carbonate is obtained by precipitation of calcium hydroxide with carbon dioxide under conditions conducive to formation of calcium carbonate having a minor proportion by weight of particles larger than 2 microns.

3. A method as defined in claim 1 and in which the calcium carbonate present in the initial suspension has a major proportion, by weight, of particles less than 2 microns in size, and the final calcium carbonate has a major proportion, by weight, of particle sizes within the range of 2 to 4 microns.

4. A method as defined in claim 1 and in which the calcium carbonate having a minor proportion by weight of particles larger than 2 microns is fed into the suspension continuously during the pre-

5 cipitation of additional calcium carbonate, and the finally produced calcium carbonate is removed from the precipitating medium continuously during the operation of the method.

- 10 5. A method of preparing calcium carbonate of controlled particle sizes comprising two steps, as follows, first, preparing a calcium carbonate suspension having a minor proportion by weight of particles larger than 2 microns, then reacting lime with carbon dioxide in the presence of this fine particle size suspension, and maintaining in this second step
- 15 an unreacted calcium hydroxide concentration within the range of about 1% to about 25% of the weight of total solids present in the suspension.

6. A method as defined in claim 1 and

in which the calcium hydroxide is added 20 to the aqueous suspension of initial calcium carbonate as an aqueous suspension at a concentration substantially equivalent to the concentration of the said calcium carbonate suspension which 25 is undergoing enlargement of the particle size, whereby the concentration of total calcium carbonate remains constant throughout the precipitation reaction.

7. Calcium carbonate whenever prepared or produced by the method claimed 30 in any of the preceding claims.

Dated this 29th day of August, 1947.  
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